PERMSELECTIVITY COEFFICIENT OF ANION EXCHANGE MEMBRANES FOR ELECTRODIALYSIS OF CITRIC ACID

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ABSTRACT

The anion exchange membrane find application in diverse process such as electrodialysis, diffusion dialysis, membrane electrolysis, reverse osmosis and membrane fuel cells, which are energy, resource, and environment saving. The development of ion-exchange membrane of high chemical, mechanical and thermal stability, which meet growing demand of the aforementioned processes, is of great importance. This paper deals with the determination of the membrane permselectivity coefficient of anion exchange membranes for concentration of citric acid using electrodialysis process. The permselectivity coefficient of three types of commercial anion exchange membranes; Neosepta ACS (Tokuyama, Japan), Neosepta AHA2 (Tokuyama, Japan) and 204UZR412 (Ionics. Inc., USA) were compared in consideration to the physicochemical data of these membranes published so far are not adequate to their industrial application particularly for citric acid concentration. The permselectivity coefficient is the ability of anion exchange membrane to allow a selective passage of citrate ions (Cit^{3-}) and chloride ions (Cl^-) under the influence of electrical potential difference. To measure the permselectivity coefficient of different types of anion exchange membrane, the experimental conditions were maintained at a constant value. The initial concentration of feed solution was maintained at 0.1M sodium citrate and 0.1M of sodium chloride. The constant current density used was 432 A/m^2 and the flow rate was 500 ml/min.

Keywords: Anion exchange membrane; Electrodialysis; Permselectivity coefficient; Citric acid.

INTRODUCTION

Separation membrane have become essential and, thus various membranes have been developed; membrane for reverse osmosis, nanofiltration, ultrafiltration, microfiltration, ion exchange membrane, membrane for medical use such as an artificial kidney, etc. (Sata, 2000). Among these membranes, ion exchange membranes are one of the most advance separation membranes. Ion exchange membranes are used in different electrochemical system of technical importance such as chlor-alkali electrolysis, electrodialysis, dialysis and fuel cells. More recently application of ion exchange membrane in liquid redox batteries has been reported (Ohya *et.al*, 1990). Electrodialysis is an electrochemical separation process in which electrically charged membranes (ion exchange membrane) and electrical potential difference are used to separate ionic species from an aqueous solution or other uncharged components (Moon *et.al*, 1998). Basically the ion exchange membranes separate cations from anion. Thus cations and anions can be separated by cation and anion exchange membrane from a low concentration to an extremely high concentration as a result of extensive studies on these membranes.

However it is difficult to separate ions with the same sign and same charge. Based on the requirement for electrodialytic concentration of seawater, many trials have been carried out, and monovalent cation exchange membrane and sulfate ion permeable membranes have been used industrially.

In recent years, the requirement for ion exchange membranes having permselectivity for specific ions have been increasing, such anion exchanges membranes to remove nitrate from groundwater (Sata, 1997). If ion exchange membrane and electrodialysis methods are found to permeate a specific ion through the membranes, the utilization of specific ion exchange membrane will further expand.

THEORY

Ion selectivity of ion-exchange membrane is quantitatively expressed in terms of permselectivity, which measure the ease with which counter ion migration occurs through an ion-exchange membrane. Permselectivity among component in a mixture through non-porous separation is governed by the difference in the affinity of respective component with the membrane and the difference of the migration speed of the component in the membrane phase (Sata, 2000). Permselectivity among anions through anion exchange membrane in electrodialysis is also governed by the affinity of anions with membranes (ion exchange equilibrium constant) and the difference of the migration speed of the respective anions (mobility ratios among the anions). To simplify the system, a standard anion is decided and the ratio of the permeated equivalent of a given anion is to that of the standard anion is compared. In general, chloride ions are used as the standard anion. When one equivalent of chloride ions permeates through the membrane, the permeated equivalent of a given anion is evaluated. The permselectivity between anion A and chloride ions, P_{Cl}^{A}, which is called as transport number of anion A relative to chloride ions, is defined by the following equation,

$$P_{Cl}^{A} = \frac{(t_A / t_{Cl})}{(C_A / C_{Cl})} \tag{1}$$

Where t_A and t_{Cl} are transport of anion A and Cl^- in the membrane phase, and C_A and C_{Cl} the concentration (equivalent) on anion A and Cl^- at the membrane surface of desalting side solution during electrodialysis, respectively. When equivalent permeated through the membrane (flux) and transport number of Ai ion in the membrane phase during electrodialysis are L_{Ai} and t_{Ai}, respectively, $t_{Ai} = L_{Ai} / \Sigma_j L$. Thus, Eq. (1) changes as follows,

$$P_{Cl}^{A} = \frac{L_A C_{Cl}}{L_{Cl} C_A} \tag{2}$$

Since L_{Ai} can be express by: $L_{Ai} = U_{Ai} C_{RAi} (dE/dx)$ {U_{Ai} is the mobility of A_i anion in the membrane phase [$cm^2/(dE/dx)s$], C_{RAi} the concentration of Ai anions in the membrane phase during electrodialysis (equiv./cm^3) and (dE/dx) the electrical potential gradient in the membrane phase}, Eq.(2) can be rearranged to

$$P_{Cl}^{A} = \frac{U_A C_{RA} C_{Cl}}{U_{Cl} C_{RCl} C_A} \tag{3}$$

The ion exchange equilibrium constant between anion A and chloride ions in the membrane, K_{Cl}^{A}, is expressed as follows,

$$K_{Cl}^{A} = \left(\frac{C_{RA} / C_{RCl}}{C_{A} / C_{Cl}} \right) \tag{4}$$

Thus, P_{Cl}^{A} is expressed by a following equation when the effect of diffusion boundary layers at the membrane-solution interfaces on P_{Cl}^{A} can be completely eliminated.

$$P_{Cl}^{A} = \frac{U_{A}}{U_{Cl}} K_{Cl}^{A} \tag{5}$$

Accordingly, P_{Cl}^{A} is the product of the ratio of mobility of anion A in the membrane phase to that of chloride ions by the ion exchange equilibrium constant between anions A and chloride ions.

The permselective coefficient is the ability of an anion exchange membrane to allow selective passage of citrate ion (Cit^{-3}) and chloride ions (Cl-) under the influence of electrical potential. If the initial concentration of (Cit^{-3}) and (Cl-) were C_{Cit}^{0} and C_{Cl}^{0} at time t of electrodialysis, the concentration of Cit^{-3} and Cl^{-1} in the diluting stream were C_{Cit}^{t} and C_{Cl}^{t} respectively. The permselective coefficient T_{Cl}^{Cit} was defined as:

$$T_{Cl}^{Cit} = \frac{\left(C_{Cit}^{0} - C_{Cit}^{t}\right) / C_{Cit}^{0}}{\left(C_{Cl}^{0} - C_{Cl}^{t}\right) / C_{Cl}^{0}} = \frac{\Delta C_{Cit}^{t} / C_{Cit}^{0}}{\Delta C_{Cl}^{t} / C_{Cl}^{0}} \tag{6}$$

Where ΔC_{Cit}^{t} and ΔC_{Cl}^{t} is the decrement of concentration of Cit^{-3} and Cl^{-1} respectively, in the diluting stream at the time t of electrodialysis.

Equation 3.2 is only valid if the volume of solution is kept constant during electrodialysis. However, in situation where the volume of diluting stream decrease due to water transport, equation 3.2 can be rewritten as:

$$T_{Cl}^{Cit} = \frac{\Delta Q_{Cit}^{t} / Q_{Cit}^{0}}{\Delta Q_{Cl}^{t} / Q_{Cl}^{0}} \tag{7}$$

Where Q_{Cit}^{0} and Q_{Cl}^{0} are the initial ionic weight of Cit^{-3} and Cl^{-1} in the diluting stream. ΔQ_{Cit}^{t} and ΔQ_{Cl}^{t} are the decrement of ionic weight of Cit^{-3} and Cl^{-1} respectively in the diluting stream at the time t of electrodialysis.

The lower permselective coefficient, the harder for Cit^{-3} ion to pass through the anion exchange membranes. This means that the degree of separation was high. A coefficient equals to one, means that Cit^{-3} and Cl^{-1} have similar ability to pass through the membranes. As a result no separation takes place

EXPERIMENTAL

The effective membrane transfer area of each cell pair was 232 cm^2. The membranes were bound to one end by an anolyte compartment and an anode, while the other end was connected to a catholyte compartment and a cathode. In the anolyte compartment, a platinized titanium anode was installed. While for the cathode, stainless steel was installed. The solution flowing through the membrane stack was regulated by spacer gasket to ensure a sheet flow was obtained. The intermembrane spacers were 1.02mm thick. The electrode spacers were 2.04mm thick. The complete membrane stack was held together by four bolts. Four peristaltic pumps were used to circulate the process streams and electrode streams. Masterflex ® pump heads 7017 and 7018 (Cole Parmer, USA) were used for electrode streams and process streams, respectively. Norprene food tubing (Cole Parmer, USA) was used for connecting the pump to the stack assembly. The electrodialysis stack was operated in a batch mode. Three storage tank and four pumps were used for continuously circulating concentrate, diluate, and electrode rinse solutions. The flow rate in the diluate and concentrate compartment was maintained at 500 ml/min. In the experiments, a 3% (w/v) sodium sulfate (electrode rinse) solution was circulated through the electrode compartments.

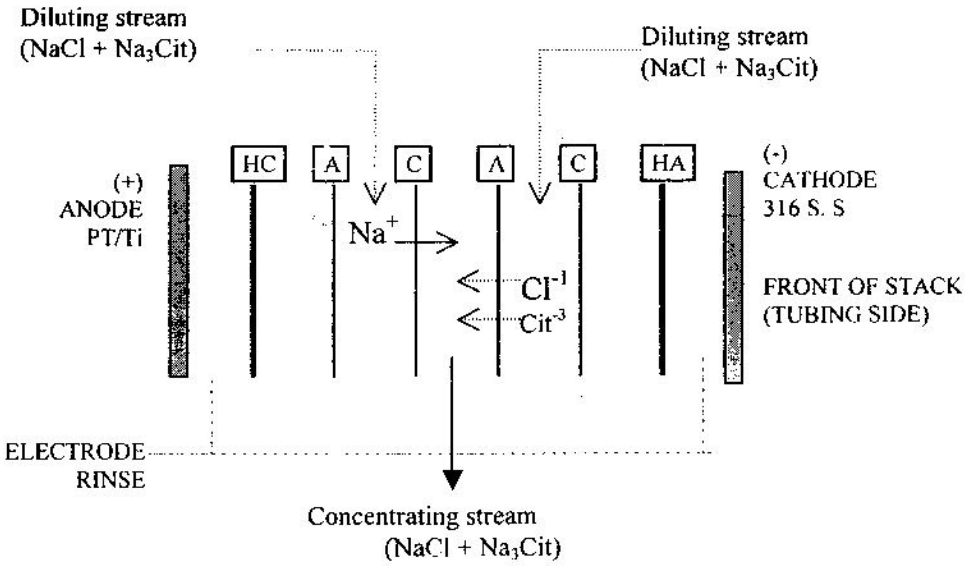


Figure 1: Experimental set up for measurement of permselective coefficient of the anion exchange membrane: C, cation exchange membrane; A, anion exchange membrane

The experimental set up to determine the permselective coefficient of anion exchange membranes is shown in Figure 1. The initial mixed solution of sodium citrate (Na_3Cit) and sodium chloride (NaCl) was placed in the concentrating and diluting tanks. The solutions were circulated individually as diluting stream and concentrating stream through circulation pumps at the flow rate of 500 ml/min. The electrode rinse solution of 0.3M sodium sulphate was circulated through both of the electrode rinse streams. Three types of anion exchange membrane were tested: Neosepta ACS (Tokuyama, Japan), Neosepta AHA2 (Tokuyama, Japan) and 204UZR412 (Ionics Inc., USA). The properties of these membranes are tabulated in Table 1.

Table 1: The properties of anion exchange membranes (Ionics Inc., USA and Tokuyama, Japan).

Membrane	204UZR412	Neosepta ACS	Neosepta AHA2
Type	Anion	Anion	Anion
Reinforcing fabric	Modacrylic	PVC	PVC
Thickness (mm)	0.57	0.18	0.15
Capacity (meq/g)	2.8	1.4	1.5
Water content (%)	36	25	34
* Area resistance ($\Omega.cm^2$)	4	2.3	2.4

- Equilibrated with a 0.1M of sodium chloride (NaCl) solution, at 25°C.

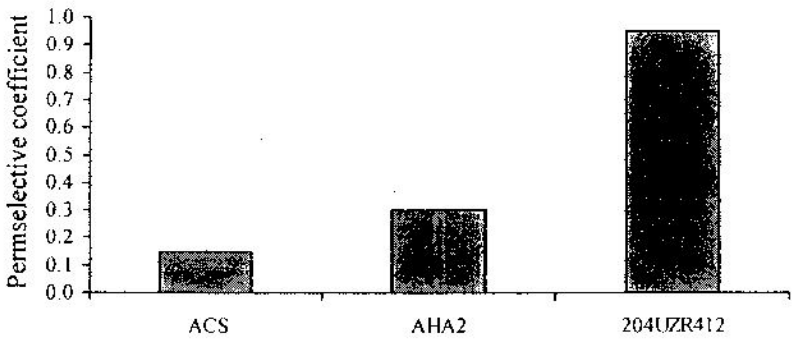
RESULT AND DISCUSSION

At the beginning and at the end of the experiment, the concentration of Cit^{-3} and Cl^{-1} ions as well as the volume in the diluting stream were measured. The Q^0_{Cit} and Q^0_{Cl} as well as Q'_{Cit} and Q'_{Cl} were evaluated, and finally the permselective coefficient was calculated according to equation (7). The concentrations of the solutions were analysed for chloride ions by the Mohr method and titration method for citrate ions. To measure permselective coefficient of different types of anion exchange membrane the experimental conditions were kept constant for the separation of sodium citrate and sodium chloride from the diluting stream to the concentrating stream. The concentration of the diluting stream contains 0.1M sodium citrate and 0.1M sodium chloride. The constant current density used was 432 A/m^2 and the flow rate in the diluting and concentrating stream was 500ml/min. The permselective coefficients for different type of anion exchange membranes are given as in Figure 2 and Table2.

Table 2: Result of the permselective coefficient of the anion exchange membranes
Neosepta ACS Neosepta AHA2204UZR412

	Types of Anion Exchange Membranes		
	Neosepta ACS (Tokuyama, Japan)	Neosepta AHA2 (Tokuyama, Japan)	204UZR412 (Ionics Inc., USA)
Permselective Coefficient	0.15	0.30	0.95

Figure 2: Permselective coefficient for some anion exchange membranes



The anion exchange membrane 204UZR412 from Ionics Inc. shows the permselective coefficient value of 0.95. The 204UZR412 anion exchange membranes were selective to the first anion having a negative valence of at least –1 and preferably from -1 to -3, such as citrate ion. This means that the 204UZR412-anion exchange membrane was selective to both weak and strong acid anions. However, the anion exchange membrane of type Neosepta AHA and Neosepta ASC with permselectivity coefficient value of 0.30 and 0.15, respective, were selective to the second anion (chloride ion), which was having a negative valence of -1 to -2. This shows that anion Neosepta AHA and Neosepta ASC was selective to strong acid anions compared to weak acid anion.

CONCLUSION

Based on the comparative study on the permselectivity coefficient of the three membranes, anion exchange membrane of type 204UZR412 shows the highest coefficient value for citrate acid. The permselectivity of anion exchange membrane towards anions depends on the nature and the properties of the membrane (Lorrain *et. al.*, 1997). It is also known that the degree of the permselectivity of the membrane is affected by the cross-linking density and the ion exchange capacity of the membrane. The ion exchange capacity for 204UZR412 membrane is 2.8 (meq/g) compared to the ion exchange capacity value of 1.4 and 1.5 (meq/g) for Neosepta ACS and Neosepta AHA2, respectively. Result of the experiment support the assumption on the correlation between ion exchange capacity of the anion exchange membrane with the permselectivity coefficient of the membrane. The result of this work serve as a basis for electrodialysis separation of citric acid.

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